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A STUDY OF THE SENSITIVITY OF COUPLED
REACTION SYSTEMS TO UNCERTAINTIES IN
RATE COEFFICIENTS. I. THEORY

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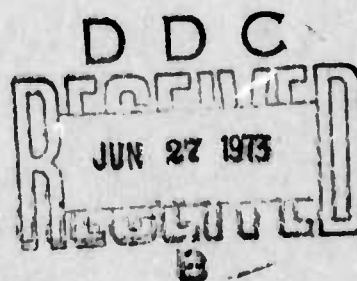
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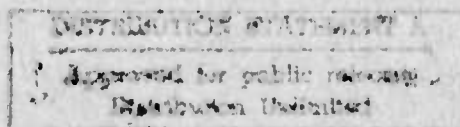
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A STUDY OF THE SENSITIVITY OF COUPLED REACTION
SYSTEMS TO UNCERTAINTIES IN RATE COEFFICIENTS
I. THEORY [+]

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ABSTRACT

A method has been developed to investigate the sensitivity of the solutions of large sets of coupled, non-linear rate equations to uncertainties in the rate coefficients. This method is based on varying all the rate coefficients simultaneously through the introduction of a parameter in such a way that the output concentrations become periodic functions of this parameter at any given time t. The concentration of the chemical species are then Fourier analysed at time t. We show via an application of Weyl's ergodic theorem that a subset of the Fourier coefficients is related to $\left\langle \frac{\partial c_i}{\partial k_\ell} \right\rangle$, the rate of change of the concentration of species i with respect to the rate constant for reaction ℓ averaged over the uncertainties of all the other rate coefficients. Thus a large Fourier coefficient corresponds to a large sensitivity, a small Fourier coefficient corresponds to a small sensitivity. The amount of numerical integration required to calculate these Fourier coefficients is considerably less than that required in test of sensitivity where one varies one rate coefficient at a time, while holding all others fixed. The Fourier method developed in this paper is not limited to chemical rate equation, but can be applied to the study of the sensitivity of any large system of coupled, non-linear differential equations with respect to the uncertainties in the modeling parameters.

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I. Introduction

Sets of coupled, non-linear rate equations arise in a number of disciplines.
A classic example is that of chemical rate equations. In the study of combustion,
air-pollution, upper atmosphere phenomena and chemical lasers as many as 100
coupled rate equations involving some 50 separate species may be needed to
account for the properties of such systems. One is then faced with the problem
of solving a large set of coupled, non-linear differential equations of the form

$$\frac{d\vec{c}}{dt} = \vec{F}\left[\vec{c}_i\{k\}\right] \tag{1.1}$$

when $\vec{c}$ is a vector of concentrations, $\{k\}$ a set of rate coefficients and $\vec{F}$ some
complicated function of the concentrations. While one may prove existence and
stability theorems for the equilibrium point[1], the only way to solve these
equations, i.e. to obtain all the species concentrations as functions of time,
is through the use of a high-speed computer.

Unfortunately, the rate coefficients (or cross sections) for many reactions
are not known with high accuracy and indeed may be uncertain by one or more
orders of magnitude. This gives rise to the very important problem of
"sensitivity" which may be defined as the effect of uncertainties in the rate
coefficients on the calculated concentrations of all the various intermediate
and product species. The uncertainty in the rate coefficients of certain
"important" reactions in the reaction scheme may have a significant effect on
the output function (for instance, concentration at time t), while uncertainties
of the same magnitude in rate coefficients of "unimportant" reaction in the
reaction scheme may hardly effect the output function. The reliability of the

output numbers clearly cannot be established without knowledge of the sensitivity of the output data to the uncertainty in the input parameters.

The problem is to find a practical method of determining the effects of the uncertainties in the rate coefficients on the solutions of the rate equations. Since we are interested in the situation where the uncertainties in the rate coefficient may be orders of magnitude, linearization schemes are not appropriate. A "brute force" method of investigating the sensitivity is not feasible as can readily be seen from the following example. Suppose we have a reaction scheme which has n coupled reactions involving m different chemical species. Let us furthermore assume that we wish to calculate the concentrations of the m species at some time t for z different values each of the 2n rate coefficients. If we now change one rate coefficient at a time while holding all the others fixed, we would have to carry out z^{2n} integrations of the rate equation (1.1) to time t. For the m different species, this procedure will give rise to a print-out of $m(z)^{2n}$ concentrations. If we know to a good accuracy the equilibrium constants for all the reactions and apply the principle of detailed balance, the number of independent rate coefficients will be reduced to n and we would have to carry out z^n integrations up to time t for each species m. In either case, for n large, it is obvious that the time and expense involved in such an analysis of sensitivity is prohibitive and the print-outs so numerous as to defy a simple analysis of the results. Clearly, one needs to devise some more powerful method for the study of sensitivity.

Our approach to this problem is to ask for a less detailed description of the effect of rate coefficient uncertainty on the output function at any given time. We vary all the rate coefficients simultaneously so as to explore the

entire space of uncertainties in the rate coefficient set {k}. As will be seen below, this turns out to be equivalent to varying a single rate coefficient and then averaging the attendant concentration changes over the uncertainties of all the other rate coefficients, where we express this uncertainty in terms of a probability distribution. Our approach is thus related to a "mean field" theory where we represent the fluctuations of the field by the uncertainties in the (n-1) rate coefficients over which we average.

To carry out this program, we relate each rate coefficient k_i to a frequency ω_i and introduce a parameter s which simultaneously varies all the rate coefficients in such a way that the concentrations <u>at a fixed time</u> become periodic functions of s. The concentrations can then be Fourier analyzed. We then show that a certain subset of these Fourier coefficients can be related to the first partial derivative of the concentration c_i of species i with respect to a rate coefficient k_ℓ averaged over the uncertainties of all the other rate coefficients. A large value of the Fourier coefficient $A_{\omega_\ell}^{(i)}$ then shows that $\left\langle \frac{\partial c_i}{\partial k_\ell} \right\rangle$ is large, i.e. the effect of a change in the ℓ'th rate coefficient on the concentration of species i is significant. Conversely, a small Fourier coefficient $A_{\omega_j}^{(i)}$ indicates that $\left\langle \frac{\partial c_i}{\partial k_j} \right\rangle$ is small, i.e. the effect of the variations of the j'th rate coefficient on the concentration of species i is small. In order to calculate these Fourier coefficients, we must integrate the rate equations numerically up to the desired time for each value of the parameter s. The number of s values which we include in our parameter set determines the accuracy to which we can calculate the Fourier coefficient; the larger the set of s values, the more accurate the determination of the Fourier coefficients.

Since we must still perform numerical integrations of the rate equations

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(1.1), the question arises why this method is to be preferred to the more direct method of varying each rate coefficient separately while keeping all others fixed. As will be shown in paper II, which deals primarily with the computer calculations, the number of integrations required by the Fourier method is $O(n^r)$ where r is a small integer (r<10) which depends upon the choice of the frequencies ω_i, i = 1,2,...,n. It can readily be verified that for n, z large, $n^r < (z)^n$. The computational economy of this method of analysis thus becomes more pronounced as n, the number of reactions, increases. The reason for this reduction in the number of required integrations up to time t is to be found in the fact that in the Fourier method we <u>sample</u> the $\vec{c}(k)$ space at a set of points determined by the values of the set {s} and the vector $\vec{\omega}$, whereas the "brute force" method involves neither sampling nor the simultaneous variation of the set of rate coefficients {k} and thus requires many more integrations of the rate equations. As will be clear from the body of the paper, this sampling in a certain sense corresponds to the averaging over all the rate coefficients. The reduction in the number of required integrations is thus intimately related to the use of a "mean field" theory.

Our results are presented in two papers, I and II. In paper I, we present the theoretical basis of our method without explicit reference to the verifying computer experiments. In paper II, we present the results of our computer calculations as well as a detailed discussion of the problems involved in such calculations.

It should be pointed out that the utility of this Fourier analysis method of testing sensitivity extends beyond the confines of chemical kinetics and beyond the confines of differential equations. Large sets of coupled, non-linear equations are used in many fields such as economics, population dynamics, weather forecasting, systems analysis, operations research, etc. for modeling

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and predictive purposes. As has been pointed out by a number of investigators, it is important that sensitivity tests be carried out on such systems to identify the critical parameters and to validate the applicability of the models. The method developed here can be applied to any set of equations,   . differential, integral, algebraic, etc., which yield an output as a complex function of many parameters. In fact, we have used an analytic function of several variables to test some of our ideas. We plan to apply this Fourier method to the analysis of other complex systems in the near future.

II. Fourier Analysis

The rate equation for coupled chemical reactions which obey the law of mass action can be written in the form

$$\frac{dc_i}{dt} = \sum_{r=1}^{n} \nu_{r,i} \left[k_r \prod_{\ell=1}^{m} c_\ell^{\nu'_{r,\ell}} - k_{-r} \prod_{\ell=1}^{m} c_\ell^{\nu''_{r,\ell}} \right] \qquad (2.1)$$

$$(i=1,\ldots,m)$$

where $c_i(k_1,\ldots,k_n;t)$ is the concentration of species i at time t, $\nu_{r,i} \equiv \nu''_{r,i} - \nu'_{r,i}$ is the stoichiometric coefficient of the species i in reaction r, with $r=1,\ldots,n$ labeling the different reactions in the reaction system, and where $k_r(k_{-r})$ is the forward (backward) rate coefficient for reaction r. The coefficients $\nu'_{r,i}$ and $\nu''_{r,i}$ are non-negative integers so that the stoichiometric coefficient ν_{ri} defined above can be positive, negative or zero. From the form of the rate equations (2.1) one can prove that the concentrations are bounded and non-negative, that they are continuous functions of the time and the rate coefficients and that an equilibrium point exists.[1]

In order to determine the effects of uncertainties in the rate coefficients $k_{\pm r}$ on the concentrations c_i at time t a systematic method for varying the k's must be developed. We define

$$k_i = k_i^{(o)} e^{u_i} \qquad (i=1,\ldots,n) \qquad (2.2)$$

and

$$u_i = f_i(\sin \omega_i s) \qquad (2.3)$$

where $k_i^{(o)}$ is the "best value" of the rate coefficient (i.e. the one which the investigator believes to be the best available value based on experiments or calculations), the "frequency" ω_i is a positive integer, s is a parameter and f_i

is a function to be determined. The introduction of the parameter u_i and the form of Eq. (2.2) permits one to effect readily order of magnitude changes in the rate coefficients. The form of equation (2.3) permits one to vary simultaneously all the rate coefficients by varying the parameter s. The rapidity of the variation is determined for each k_i by the magnitude of the ω_i's. The ω_i are chosen to be positive integers in order that the concentrations at a fixed time t become periodic functions of s with period 2π:

$$c_i(s;t) = c_i(s + 2\pi;t) \tag{2.4}$$

In the development to follow we suppress this dependence of the concentrations on time, it being understood that the analysis is carried out for a fixed time t.

The concentration as a function of s describes a closed path. That is, for each i and for every value of s we obtain a point in $\vec{k}$ space with value $c_i(\vec{k})$; as s changes by 2π we return to the same values of $\vec{k}$ and $\vec{u}$, [see eqs. (2.2) and (2.3)], and, from equation (2.4), to the same value $c_i(s)$. Since $c_i(s)$ is periodic on 2π we may expand it in a Fourier series

$$c_i(s) = \frac{A_0^{(i)}}{2} + \sum_{r=1}^{\infty} \left(A_r^{(i)} \sin rs + B_r^{(i)} \cos rs \right) \quad . \tag{2.5}$$

In the analysis presented below we are interested only in the Fourier sine coefficients A_r that correspond to the original input frequencies ω_i, i.e. the coefficients given by

$$A_{\omega_\ell}^{(i)} = \frac{1}{\pi} \int_0^{2\pi} c_i(s) \sin \omega_\ell s \, ds \quad . \tag{2.6}$$

$$\ell = 1, 2, \ldots, n$$

We now wish to relate the Fourier coefficients $A_{\omega_\ell}^{(i)}$ to the effect of the

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variation of the rate coefficients k_r and the concentrations c_i. In order to do this it is necessary to relate the s- space integral of Eq. (2.6) to a n-dimensional integral over the entire $\vec{u}$ space. It can be shown that if the entire $\vec{u}$ space is covered densely as s is varied, then the integrals over the s- space and the $\vec{u}$ space yield identical results. This is just a statement of the ergodic theorem which permits one to equate time and phase space averages in statistical mechanics.[2] If the frequencies ω_i in Eq. (2.3) were chosen to be incommensurate, then the function $c_i(s)$ i.e. the concentration as a function of the parameter s, would be an almost periodic function. This implies that the path in the space $R^n(\vec{\theta})$, where the θ's are defined by

$$\theta_i = \omega_i s \qquad (\text{mod } 2\pi) \qquad \qquad (2.7)$$

returns arbitrarily close to any initial point as $s \longrightarrow \infty$. One could then equate the s- space integral with the integral over the n- dimensional $\vec{\theta}$ space as was first proved by Weyl.[3] However, the use of an incommensurate set of frequencies ω_i in Eq. (2.3) would require that the numerical evaluation of the Fourier coefficients A_{ω_ℓ} of Eq. (2.6) be carried out over an infinite period. This clearly is not a feasible procedure on any known computer.

It is for this reason that we introduce integer frequencies ω_i in Eq. (2.3). Their use leads to a finite period (0 to 2π) analysis which can readily be handled on a computer. This will give rise to an error in the analysis since now the "phase point" will no longer densely cover the $\vec{u}$ space as s is varied and the s-space and $\vec{u}$ space integrals therefore do not yield identical results.

Let us for the moment ignore this error and use Weyl's theorem for our periodic function c(s). We write

$$A_{\omega_\ell}^{(i)} = \frac{2}{(2\pi)^n} \int_0^{2\pi} \cdots \int_0^{2\pi} \prod_{j=1}^{n} d\theta_j \, c_i(\theta_1,\ldots,\theta_n) \sin \theta_\ell \qquad . \qquad (2.8)$$

This expression can be put in a more suggestive form as follows. The ℓ'th integral is rewritten by integration by parts as

$$\frac{1}{2\pi} \int_0^{2\pi} d\theta_\ell \, c(\theta_1 \ldots \theta_n) \sin \theta_\ell = \frac{1}{2\pi} \int_0^{2\pi} d\theta_\ell \, \frac{\partial c}{\partial \theta_\ell} \cos \theta_\ell \qquad (2.9)$$

where the boundary term has vanished by the periodicity of the integrand. The use of Eq.(2.9) then permits us to rewrite Eq.(2.8) as

$$A_{\omega_\ell}^{(i)} = \frac{2}{(2\pi)^n} \int_0^{2\pi} \cdots \int_0^{2\pi} \prod_{j=1}^{n} d\theta_j \, \frac{\partial c_i}{\partial \theta_\ell} \cos \theta_\ell \qquad (2.10)$$

The $\vec{\theta}$ space integral must now be related to the $\vec{u}$ space integral. The transformation is (see Eqs. (2.3) and (2.7))

$$du_j = \frac{\partial f_j(\sin \theta_j)}{\partial \sin \theta_j} \cos \theta_j \, d\theta_j \qquad (2.11)$$

where we require that f_j be a monotonic function of its argument. Then

$$A_{\omega_\ell}^{(i)} = \frac{2}{\pi^n} \int_{f_1(-1)}^{f_1(+1)} \cdots \int_{f_n(-1)}^{f_n(+1)} \frac{\prod\limits_{j=1}^{n} du_j \cos \theta_\ell \, \dfrac{\partial c_i}{\partial u_\ell}}{\prod\limits_{j \neq \ell}^{n} \cos \theta_j \, \dfrac{\partial f_j(\sin \theta_j)}{\partial \sin \theta_j}} \qquad (2.12)$$

In order to obtain a definite relation between $A_{\omega_\ell}^{(i)}$ and $\partial c_i / \partial u_\ell$ we must choose some particular form for the function $f_j(\sin \theta_j)$. There are several choices which lead to useful expressions for the $A_{\omega_\ell}^{(i)}$; as will be seen below, a particularly advantageous choice is to set

$$\frac{\partial f_j(\sin \theta_j)}{\partial \sin \theta_j} \cos^2 \theta_j = \frac{1}{a_j} , \qquad (2.13)$$

where a_j is a parameter. The use of Eq. (2.13) in Eq. (2.12) leads to

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$$A_{\omega_\ell}^{(i)} = \frac{2}{a_\ell \pi^n} \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \prod_{j=1}^{n} du_j \, a_j \cos \theta_j \frac{\partial c_i}{\partial u_\ell} \quad . \tag{2.14}$$

Integration of Eq. (2.13) yields

$$f_j(\sin \theta_j) = u_j = \frac{1}{2a_j} \ln \left[\frac{1 + \sin \theta_j}{1 - \sin \theta_j} \right] \tag{2.15}$$

and also indicates the range of integration in Eq. (2.14). Expressing $\cos \theta_j$ as a function of u_j from Eq. (2.15) gives for Eq. (2.14)

$$A_{\omega_\ell}^{(i)} = \frac{2}{a_\ell \pi^n} \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \prod_{j=1}^{n} du_j \, \frac{a_j}{\cosh a_j u_j} \, \frac{\partial c_i}{\partial u_\ell} \quad . \tag{2.16}$$

Since

$$\int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \prod_{j=1}^{n} du_j \, \frac{a_j}{\cosh a_j u_j} = \pi^n \tag{2.17}$$

we obtain as our final result

$$A_{\omega_\ell}^{(i)} = \frac{2}{a_\ell} \, \langle \partial c_i / \partial u_\ell \rangle \tag{2.18}$$

where the bracket in Eq. (2.18) is defined by

$$\langle Y(u_1, \ldots, u_n) \rangle = \frac{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{+\infty} \prod_{i=1}^{n} p(u_j; a_j) \, Y(u_1, \ldots, u_n) \, du_i}{\int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \prod_{i=1}^{n} p(u_j; a_j) \, du_i} \tag{2.19}$$

and

$$p(u_j; a_j) = \frac{a_j}{\cosh a_j u_j} \quad . \tag{2.20}$$

The function $p(u_j; a_j)$ can be interpreted as a distribution function in $\vec{u}$ space which weights the uncertainty in the rate coefficients. Equation (2.18) is the

desired relation between the Fourier coefficient $A_{\omega_\ell}^{(i)}$ and the change in the concentration of species i with a change in the ℓ'th rate coefficient, $\partial c_i / \partial u_\ell$, averaged over the changes of all the other rate coefficients.

The particular form of f_j ($\sin \theta_j$) that we have chosen, Eq. (2.15), has lead to a weight function $p(u_j; a_j)$ for each rate coefficient, Eq. (2.20), which has several convenient properties. As a function of u_j, the function $p(u_j; a_j)$ is symmetrically bell shaped about $u_j = 0$ corresponding to $k_j = k_j^{(o)}$, the "best" value of the rate coefficient k_j. As a_j, which is a parameter at our disposal, is increased, the weight function $p(u_j; a_j)$ narrows about $u_j = 0$; this corresponds to a decreased spread in the values of the rate constant k_j, i.e. it corresponds to a narrower range of the uncertainty of k_j around $k_j^{(o)}$. In the limit as $a_j \rightarrow \infty$, one obtains

$$\lim_{a_j \rightarrow \infty} p(u_j; a_j) = \pi \delta(u_j) \tag{2.21}$$

where $\delta(x)$ is the delta function of argument x which implies that the rate constant is known with certainty to be $k_j^{(o)}$. When some information is available on the spread and distribution about the value of the rate coefficient k_j about its "best" value $k_j^{(o)}$, one can determine the a_j through the standard deviation of the values in $\vec{u}$ space

$$\langle u_j^2 \rangle = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{u_j^2 \, a_j \, du_j}{\cosh a_j u_j} = \frac{\pi}{4} \frac{1}{a_j^2} \tag{2.22}$$

from which it follows that

$$a_j = \frac{\pi}{2} \frac{1}{\langle u_j^2 \rangle^{1/2}} \qquad \qquad . \tag{2.23}$$

The parameter a_j thus permits us to introduce explicitly the spread of uncertainties in the values of the rate coefficients into our analysis.

To calculate the Fourier coefficients $A_{\omega_\ell}^{(i)}$ we must first choose a suitable set of ω_j's and a_j's. What constitutes a "suitable" set of ω's will be discussed in the next section in conjunction with the error analysis and in more detail in paper II. The set of ω_j's defines the u_j's as a function of s according to Eqs. (2.3), (2.7) and (2.15). For each value of s one obtains a value of the concentration $c_i(k_1,\ldots,k_n)$. In principle one can then compute the $A_{\omega_\ell}^{(i)}$ to any desired accuracy by taking enough values of s,

$$s = \frac{2\pi q}{m} , \quad q = 1,2,\ldots,m, \tag{2.24}$$

where m is some integer.

It is important to point out that our main interest is in identifying those rate coefficients whose variation significantly effects the concentration c_i of a species i at time t, and those rate coefficients whose variation has only a minimal effect on the species concentration c_i. Thus if one of the Fourier coefficients, say $A_{\omega_j}^{(i)}$, is one or more orders of magnitude larger than all other coefficients $A_{\omega_\ell}^{(i)}$, $\ell = 1,2,\ldots,n$, $(\ell \neq j)$, than the variation of the j'th rate coefficient k_j, clearly has a larger effect on the concentration $c_i(t)$ than the variation of the other rate coefficients. If on the other hand all the coefficients $A_{\omega_\ell}^{(i)}$, $\ell = 1,2,\ldots,n$, are of the same order or magnitude, then the concentration of species i at time t, $c_i(t)$, is effected essentially equally by the variation of any of the rate coefficients k_ℓ.

One problem with the above analysis must be pointed out. The Fourier coefficient $A_{\omega_\ell}^{(i)}$ of Eq. (2.18) may be small either because $\partial c_i/\partial u_\ell$ is small over

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the whole range of integration of Eq. (2.19), which is the case discussed above, or because $\partial c_i/\partial u_\ell$ changes sign one or more times in the range of integration. Thus, a small value of $A_{\omega_\ell}^{(i)}$ does not necessarily imply that the concentration c_i is insensitive to changes in the rate coefficients. The remedy for this difficulty would be to find a relation between the Fourier coefficients, or a combination of Fourier coefficients, and an everywhere positive (or everywhere negative) function of the rate of change of the concentrations with rate coefficients, such as for instance $\langle (\partial c_i/\partial u_\ell)^2 \rangle$. We have, however, not been able to establish such a relationship and it seems doubtful that a simple relationship of this form exists. In carrying out computer calculations it should, however, not be too difficult to verify whether $\partial c_i/\partial u_\ell$ at any given time t is monotone or not in the range of integration over the $\vec{u}$ space.

Thus while one can assert that a large $\Lambda_{u_\ell}^{(i)}$ implies high sensitivity of the concentration of species i with respect to changes in the rate coefficient k_ℓ, the converse statement does not necessarily follow without checking on the monotonicity of $\partial c_i/\partial u_\ell$ as discussed above.

III. Choice of the Frequencies ω_i.

As we have mentioned above, the application of Weyl's theorem in going from s space, Eq. (2.6), to the $\vec{u}$ space, Eq. (2.16), via the $\vec{\theta}$ space, Eq. (2.8), must lead to an error in the analysis since we use commensurate (integer) frequencies. This error can be minimized by a judicious choice of the integer frequencies ω_i and the number and magnitude of the m values of the parameter s given by Eq. (2.24). We limit ourselves here to some qualitative remarks which will, however, clearly indicate the nature of the problem.

The integer frequencies ω_i lead, according to Eqs. (2.7) and (2.24), to a covering of the n dimensional $\vec{\theta}$ space by an array of points as q takes on its integer values q=1,2,...,m. Clearly one obtains a better coverage of the $\vec{\theta}$ space and thus reduces the error in applying Weyl's theorem if one can increase the density of points in the n-dimensional hypercube and if one can distribute the points uniformly within the space. Since $\vec{\omega}$ and q are both integer, the points $\vec{\omega} \cdot$ s (mod 2π) will form a regular lattice in $\vec{\theta}$ space. Our objective will be to make this point lattice, which is completely generated by a unit cell, as uniform as possible in all n directions by a judicious choice of the ω's. As our measure of uniformity we take a hypercubic unit cell. Without further information about the behavior of the output function this seems the most reasonable choice.

For a fixed number m of s points, chosen for computational convenience, we will try to find a vector $\vec{\omega}$ (of the infinite set of $\vec{\omega}$'s) which gives rise to a hypercubic unit cell. Once having done this we can assert, without loss of generality, that $\frac{2\pi\vec{\omega}}{m}$ lies along one edge of this hypercubic unit cell whose length is $\frac{2\pi|\vec{\omega}|}{m}$. There are now two ways to compute the volume V of the

unit cell. In the n dimensional θ space, it follows from the above construction that

$$V = \left(\frac{2\pi |\vec{\omega}|}{m} \right)^n \tag{3.1}$$

But we also know that the total volume of the n-dimensional θ space is $(2\pi)^n$. Since there are m unit cells in that space, it follows that

$$V = \frac{1}{m} (2\pi)^n \tag{3.2}$$

Equating (3.1) and (3.2) then yields

$$|\vec{\omega}| = m^{\frac{n-1}{n}} \tag{3.3}$$

for the relation between the minimum length of the vector $\vec{\omega}$, the dimension n and the number of s points, m, for a point lattice composed of hypercubic unit cells.

The condition expressed in equation (3.3) yields important insight into the judicious choice of the frequencies ω_i. For systems with large dimensions, i.e. a large number n of rate coefficients (or coupling parameters in general), $|\vec{\omega}|$ approaches m. Thus, the choice of the number m of s points for the numerical computation determines the value of $\vec{\omega}$ and thus guides one in the choice of the ω_i's. Since one would expect the error in the analysis due to the use of integer frequencies ω_i to be of order 1/m, i.e. inversely proportional to the number of unit cells, it is evident that one should choose a large value of m to carry out the calculations. This in turn implies from Eq. (3.3) a large $|\vec{\omega}|$.

The analysis leading to Eq. (3.3) is based on the construction of unit cells which are exact hypercubes. Since $|\vec{\omega}|$, m and n are all integers it may

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not be possible to fulfill condition (3.3) exactly for all (arbitrary) choices of m and n. It is easy to show this. Let us, for instance, square both sides of Eq. (3.3) and let n = 5. We are then required to find an integer m such that we can express a sum of n squares, $|\vec{\omega}|^2$, as $m^{8/5}$. Clearly, this is possible, if at all, only for certain special values of m. To be more realistic, we should weaken our criteria for uniformity of the point lattice by stipulating unit cells which are as close as possible to hypercubic and then rewrite Eq. (3.3) as

$$|\vec{\omega}| \simeq n^{\frac{n-1}{n}} \tag{3.4}$$

For n $\gg$ 1, for which both (3.3) and (3.4) reduce to $|\vec{\omega}| \simeq m$, it should be possible to obtain a more nearly exact hypercubic unit cell.

The question as to the "optimum" choice of the ω's has been considered by a number of authors, using a different approach from that presented above, in connection with the general problem of the approximate evaluation of multi-dimensional integrals via discrete summations[4]. Korobov's book has tables of ω_i's for a given number of points m (for m prime) and dimension n up to n = 10. These tables are reprinted in the book by A. H. Stroud. It is interesting and comforting to note that although these tables were computed from completely different criteria than those employed by us, the Korobov $\vec{\omega}$'s indeed generate hypercubic unit cells to a very good approximation for all his sets of $\vec{\omega}$ for which we have carried out the appropriate calculations.

Korobov's analysis of the error in the use of integer frequencies yields explicit prescriptions for calculating the "optimum" set of ω_i's as given in his tables. Our approach presented above does not yield such an explicit algorithm. We plan to develop such an algorithm and then compare our sets of $\vec{\omega}$ with those of Korobov in a subsequent publication.

As stated above, if one wishes to decrease the error in the integer frequency analysis, one should use a large number m of s points and thus a large $|\vec{\omega}|$. It can readily be verified from Eq. (2.6) that for large ω_i one needs to evaluate $c(s)$ for a larger number of s values in order to obtain an accurate value for the Fourier coefficient $A_{\omega_\ell}^{(i)}$. This requires more extensive computer calculations. A reasonable compromise between these two effects needs to be adopted.

The transformation from $\vec{u}$ space to $\vec{\theta}$ space as given by Eqs. (2.3) and (2.7) will also effect the error term since the specific transformation which is chosen determines the rate of change of the function $c(s)$ as a function of s. We are faced here with an interesting problem in compensating effects. Either the transformation $u_i = u_i(\theta)$ is singular or the weight function $p(u_i;a_i)$ is singular at one or more values of u_i. For the chosen transform it is readily verified from Eqs. (2.15) and (2.20) that u_i diverges at $\theta = \pi/2$ and $\theta = 3\pi/2$, but at these points $p(u_i;a_i) = 0$. This same effect will be found for any transformation and its associated weight function. Thus in the regions of $\vec{\theta}$ space where the transformation is divergent the associated weight function will always compensate. We are therefore led to expect that the choice of the transformation function will not significantly effect the final numerical results. This is born out by the data presented in paper II.

Acknowledgements

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